Inorg. Chem. **2005**, *44*, 2381–2390

Reactivity of Rhenium(V) Oxo Schiff Base Complexes with Phosphine Ligands: Rearrangement and Reduction Reactions

Paul D. Benny, Jenny L. Green, Hendrik P. Engelbrecht, Charles L. Barnes, and Silvia S. Jurisson*

Department of Chemistry, University of Missouri, 125 Chemistry Building, 601 S. College Avenue, Columbia, Missouri 65211

Received September 22, 2004

The symmetric rhenium(V) oxo Schiff base complexes *trans*-[ReO(OH_2)($acac_2$en)]Cl and *trans*-[ReOCl($acac_2$pn)], where $acac_2$en and $acac_2$pn are the tetradentate Schiff base ligands *N*,*N*′-ethylenebis(acetylacetone) diimine and *N*,*N*′-propylenebis(acetylacetone) diimine, respectively, were reacted with monodentate phosphine ligands to yield one of two unique cationic phosphine complexes depending on the ligand backbone length (en vs pn) and the identity of the phosphine ligand. Reduction of the Re(V) oxo core to Re(III) resulted on reaction of *trans*-[ReO(OH_2)($acac_2$en)]Cl with triphenylphosphine or diethylphenylphosphine to yield a single reduced, disubstituted product of the general type *trans*-[$Re^{III}(PR_3)_2$($acac_2$en)]$^+$. Rather unexpectedly, a similar reaction with the stronger reducing agent triethylphosphine yielded the intramolecularly rearranged, asymmetric *cis*-[$Re^{V}O(PEt_3)$($acac_2$en)]$^+$ complex. Reactions of *trans*-[$Re^{V}O$($acac_2$pn)Cl] with the same phosphine ligands yielded only the rearranged asymmetric *cis*-[$Re^{V}O(PR_3)$($acac_2$pn)]$^+$ complexes in quantitative yield. The compounds were characterized using standard spectroscopic methods, elemental analyses, cyclic voltammetry, and single-crystal X-ray diffraction. The crystallographic data for the structures reported are as follows: *trans*-[$Re^{III}(PPh_3)_2$($acac_2$en)]PF_6 ($H_{48}C_{48}N_2O_2P_2$-Re·PF_6), **1**, triclinic ($P\bar{1}$), a = 18.8261(12) Å, b = 16.2517(10) Å, c = 15.4556(10) Å, α = 95.522(1)°, β = 97.130(1)°, γ = 91.350(1)°, V = 4667.4(5) Å^3, Z = 4; *trans*-[$Re^{III}(PEt_2Ph)_2$($acac_2$en)]PF_6 ($H_{48}C_{32}N_2O_2P_2$Re·PF_6), **2**, orthorhombic (*Pccn*), a = 10.4753(6) Å, b =18.4315(10) Å, c = 18.9245(11) Å, V = 3653.9(4) Å^3, Z = 4; *cis*-[$Re^{V}O(PEt_3)$($acac_2$en)]PF_6 ($H_{33}C_{18}N_2O_3$PRe·1.25PF_6), **3**, monoclinic (*C*2/*c*), a = 39.8194(15) Å, b = 13.6187(5) Å, c = 20.1777(8) Å, β = 107.7730(10)°, V = 10419.9(7) Å^3, Z = 16; *cis*-[$Re^{V}O(PPh_3)$($acac_2$pn)]PF_6 ($H_{35}C_{31}N_2O_3$-PRe·PF_6), **4**, triclinic ($P\bar{1}$), a = 10.3094(10) Å, b =12.1196(12) Å, c = 14.8146(15) Å, α = 105.939(2)°, β = 105.383(2)°, γ = 93.525(2)°, V = 1698.0(3) Å^3, Z = 2; *cis*-[$Re^{V}O(PEt_2Ph)$($acac_2$pn)]PF_6 ($H_{35}C_{23}N_2O_3$PRe·PF_6), **5**, monoclinic ($P2_1/n$), a = 18.1183(18) Å, b = 11.580(1) Å, c = 28.519(3) Å, β = 101.861(2)°, V = 5855.9(10) Å^3, Z = 4.

Introduction

Interest in the chemistry of Re(V) oxo complexes stems from their applications to catalysis and therapeutic nuclear medicine. Re(V) oxo Schiff base complexes based on the tetradentate salicylaldehyde-derived Schiff base ligands (e.g., sal_2en and sal_2pn) have been investigated extensively.[1−9] Re(V) oxo Schiff base complexes based on the tetradentate acetylacetone-derived Schiff base ligands (e.g., $acac_2$en and $acac_2$pn) have not received as much attention.[1,7,10,11] We

* Author to whom correspondence should be addressed. E-mail: JurissonS@missouri.edu. Phone: 573-882-2107. Fax: 573-882-2754.

(1) Middleton, A. R.; Masters, A. F.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1979**, 542−546.
(2) Tisato, F.; Refosco, F.; Mazzi, U.; Bandoli, G.; Dolmella, A. *Inorg. Chim. Acta* **1989**, *164*, 127−135.
(3) Banbery, H. J.; McQuillan, F.; Hamor, T. A.; Jones, C. J.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1989**, 1405−1407.
(4) Banbery, H. J.; McQuillan, F. S.; Hamor, T. A.; Jones, C. J.; McCleverty, J. A. *Inorg. Chim. Acta* **1990**, *170*, 23−26.
(5) Tisato, F.; Refosco, F.; Mazzi, U.; Bandoli, G.; Nicolini, M. *Inorg. Chim. Acta* **1991**, *189*, 97−103.
(6) Hermann, W. A.; Rauch, M. U.; Artis, G. R. J. *Inorg. Chem.* **1996**, *35*, 1988−1991.
(7) Bottomley, L. A.; Wojciechowski, P. E.; Holder, G. N. *Inorg. Chim. Acta* **1997**, *255*, 149−155.
(8) van Bommel, K. J. C.; Verboom, W.; Kooijman, H.; Spek, A. L.; Reinhoudt, D. N. *Inorg. Chem.* **1998**, *37*, 4197−4203.
(9) Bereau, V. M.; Khan, S. I.; Abu-Omar, M. M. *Inorg. Chem.* **2001**, *40*, 6767−6773.
(10) Carrondo, M. A. A. F. d. C. T.; Middleton, A. R.; Skapski, A. C.; West, A. P.; Wilkinson, G. *Inorg. Chim. Acta* **1980**, *44*, L7−L8.
(11) Benny, P. B.; Barnes, C. L.; Piekarski, P. M.; Lydon, J. D.; Jurisson, S. S. *Inorg. Chem.* **2003**, *42*, 6519−6527.

10.1021/ic048670j CCC: $30.25
Published on Web 02/17/2005

recently reported on the syntheses of the monomeric Re(V) oxo Schiff base complexes with $acac_2en$ (*N*,*N*′-ethylenebis-(acetylacetone) diimine) and $acac_2pn$ (*N*,*N*′-propylenebis-(acetylacetone) diimine).[11] In this paper, we report on the reactivity of the monomeric Re(V) oxo Schiff base complexes *trans*-[$ReO(OH_2)(acac_2en)$]Cl and *trans*-[$ReOCl(acac_2pn)$] with tertiary phosphines.

Our interest in the Re(III) complexes stems from the expectation that d^4 Re(III) complexes will be kinetically more inert than d^2 Re(V) complexes and, thus, may be useful for radiotherapeutic applications. Two Re radioisotopes, ^{186}Re and ^{188}Re, have potential utility in therapeutic radiopharmaceuticals.[12,13] The impetus for this work arose from our interest in targeted radiotherapy using the radionuclides ^{186}Re (90 h $t_{1/2}$, 1.02 MeV β^-, 137 keV γ (7%)) and ^{188}Re (17 h $t_{1/2}$, 2.11 MeV β^-, 155 keV γ (15%)) and is based on earlier promising work on ^{99m}Tc-based diagnostic agents. Rhenium is the third row congener of Tc, and thus their chemistry is closely related, making them a matched pair for formulation of radiodiagnostic (^{99m}Tc) and radiotherapeutic ($^{186/188}Re$) agents. In the earlier work, Tc(V) oxo Schiff base complexes analogous to those reported in this paper (*trans*-[TcOX(Schiff base)]$^{0/+}$ (X = Cl^-, OH_2)) were shown to react with phosphines to yield Tc(III) complexes of the type *trans*-[Tc-$(PR_3)_2$(Schiff base)]$^+$ that showed reversible Tc(III)/Tc(IV) and Tc(III)/Tc(II) redox couples.[14−16] This chemistry led to the development of a series of Tc(III) Schiff base phosphine complexes, referred to as the Q-series, as potential myocardial imaging agents.[17,18] The Q-series of complexes were more recently evaluated for utility in assessing multidrug resistance to chemotherpeutic agents.[19] The reactivity of the Re(V) oxo Schiff base complexes with phosphines resulted in the formation of the Re(III) analogues to the Tc(III) complexes in some cases and to rearranged Re(V) oxo complexes in other cases, with the product dependent on both the Schiff base ligand and the phosphine. The Re(V) and Re(III) Schiff base phosphine complexes synthesized were fully characterized, including single-crystal X-ray diffraction and cyclic voltammetric analysis.

Results and Discussion

The reactions of tertiary phosphine ligands (PR_3) with symmetric rhenium(V) oxo N_2O_2 acetylacetone-derived Schiff base complexes of the type *trans*-[$Re^{V}OX(L)$]$^{0/+}$, where X = Cl^- or OH_2 and L = $acac_2en$ or $acac_2pn$, yielded some rather unexpected results. The reactions of simple alkyl- and arylphosphines with the Re(V) complexes resulted in the formation of two different types of complexes containing coordinated phosphine ligands. Depending on the Schiff base ligand ($acac_2en$ or $acac_2pn$) and the phosphine ligand (PPh_3, PEt_2Ph or PEt_3), either a reduced and disubstituted trans bis-(phosphine) Re(III) or a cis monosubstituted phosphine Re-(V) oxo complex was isolated (Figure 1). The Re(III) complexes resulted from the reduction of the metal center, possibly through yl-oxygen atom abstraction by the phosphine ligand following initial phosphine coordination trans to the oxo group, to yield symmetric complexes of the type *trans*-[$Re^{III}(PR_3)_2(L)$]$^+$ and the phosphine oxide. The Re(V) oxo complexes resulted from phosphine substitution of the trans ligand (Cl^- or H_2O) and intramolecular rearrangement to generate asymmetric complexes of the type *cis*-[$Re^{V}O$-$(PR_3)(L)$]$^+$. The specific type of substituted complex isolated, either through reduction or rearrangement, appears to be dependent on the nature of the Schiff base ligand and the phosphine ligand and may be the result of the kinetics of rearrangement versus reduction.

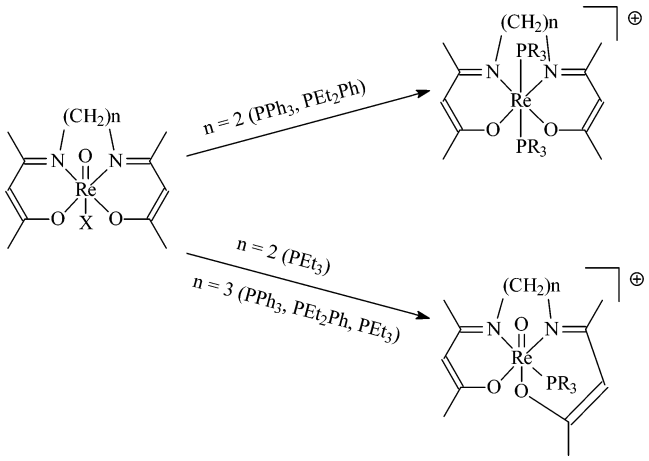


Figure 1. Formation of rhenium(III) complexes or asymmetric rhenium-(V) phosphine complexes.

The general synthesis of compounds **1**−**6** employed two different methods that each yielded single products. One method involved a two step in situ approach, where 2 equiv of the ligand ($acac_2en$ or $acac_2pn$) was reacted with a common Re(V) starting material, [*n*-Bu_4N][$ReOCl_4$], followed by the addition of 4 equiv of phosphine ligand. In this approach, the yields of **1**−**6** depended on the percent of rhenium complexation (40−50%) with the Schiff base ligand, which was essentially the same as that observed if the Re-(V) Schiff base complex were isolated.[11] The second method involved prior isolation of the Re(V) oxo Schiff base complex, followed by direct reaction with the phosphine ligands. The Re(V) Schiff base complexes utilized, *trans*-[$ReO(OH_2)(acac_2en)$]Cl and *trans*-[$ReOCl(acac_2pn)$], were prepared as previously reported.[11] Reaction of the Re(V) oxo Schiff base complexes directly with the phosphine ligands (4 equiv for **1** and **2**; 1 equiv for **3**−**6**) resulted in compounds **1**−**6** in excellent yields and higher purity than the two-step in situ method. The two-step in situ method resulted in

(12) Heeg, M. J.; Jurisson, S. S. *Acc. Chem. Res*. **1999**, *32*, 1053−1060.
(13) Volkert, W. A.; Hoffman, T. J. *Chem. Rev*. **1999**, *93*, 1137−1156.
(14) Jurisson, S.; Lindoy, L. F.; Dancey, K. P.; McPartlin, M.; Tasker, P. A.; Uppal, D. K.; Deutsch, E. *Inorg. Chem*. **1984**, *23*, 227−231.
(15) Jurisson, S. S.; Dancey, K.; McPartlin, M.; Tasker, P. A.; Deutsch, E. *Inorg. Chem*. **1984**, *23*, 4743−4749.
(16) Ichimura, A.; Heineman, W. R.; Deutsch, E. *Inorg. Chem*. **1985**, *24*, 2134−2139.
(17) Marmion, M. E.; Woulfe, S. R.; Neumann, W. L.; Nosco, D. L.; Deutsch, E. *Nucl. Med. Biol*. **1999**, *26*, 755−770.
(18) Rosetti, C.; Vanoli, G.; Paganelli, G.; Kwiakowski, M.; Zito, F.; Colombo, F.; Bonino, C.; Carpinelli, A.; Casati, R.; Deutsch, K.; Marmion, M.; Woulfe, S. R.; Lunghi, G.; Deutsch, E.; Fazio, F. *J. Nucl. Med*. **1994**, *35*, 1571−1580.
(19) Crankshaw, C. L.; Marmion, M.; Luker, G. D.; Rao, V.; Dahlheimer, J.; Burleigh, B. D.; Webb, E.; Deutsch, K. F.; Piwnica-Worms, D. *J. Nucl. Med*. **1998**, *39*, 77−86.

Table 1. X-ray Crystal Data, Data Collection Parameters, and Refinement Parameters for **1**−**5**

	1	2	3	4	5
formula	$C_{48}H_{46}N_2O_2P_2Re^+PF_6^-\cdot 0.5H_2O$	$C_{32}H_{48}N_2O_2P_2Re^+PF_6^-$	$H_{33}C_{18}N_2O_3PRe\cdot 1.25PF_6$	$C_{31}H_{35}N_2O_3PRe^+PF_6^-\cdot CH_2Cl_2$	$C_{47}H_{74}N_4O_7P_2Re_2\cdot 2PF_6$
fw	1085.99	885.83	723.85	893.21	1531.38
cryst system	Triclinic	orthorhombic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	Pccn	$C2/c$	$P\bar{1}$	$P2_1/n$
a (Å)	18.8261(12)	10.4753(6)	39.8194(15)	10.3094(10)	18.1183(18)
b (Å)	16.2517(10)	18.4315(10)	13.6187(5)	12.1196(12)	11.580(1)
c (Å)	15.4556(10)	18.9245(11)	20.1777(8)	14.8146(15)	28.519(3)
α (deg)	95.522(1)	90	90	105.939(2)	90
β (deg)	97.130(1)	90	107.733(1)	105.383(2)	101.861(2)
γ (deg)	91.350(1)	90	90	93.525(2)	90
V (Å^3)	4667.4(5)	3653.9(4)	10419.9(7)	1698.0(3)	5855.9(10)
Z	4	4	16	2	4
ρ_{calc} (g/cm^3)	1.545	1.610	1.846	1.747	1.737
T (K)	173	173(2)	173	173	173
μ (mm^{-1})	2.772	3.519	3.820	3.820	4.327
λ source (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
$R(F)^a$	0.0377	0.0197	0.0355	0.0277	0.0305
$R_w(F)^{2\,a}$	0.1007	0.0430	0.0945	0.0701	0.0675
GoF	1.049	1.036	1.035	1.073	1.040

[a] $R = (\Sigma||F_o| - |F_c||/\Sigma|F_o|)$. $R_w = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w(|F_o^2|^2]^{1/2}$.

unidentified byproducts, resulting from the reaction of unreacted rhenium starting material with the phosphine ligand to form Re(IV) or Re(V) chloro−phosphine complexes, which were separated using chromatographic methods.

Reaction of *trans*-[ReO(OH$_2$)(acac$_2$en)]Cl with phosphine ligands resulted in either the reduced Re(III) core or the rearranged Re(V) oxo complex. Aryl-containing phosphine ligands (i.e., PPh_3 or PEt_2Ph) reacted with *trans*-[Re^{V}O(OH$_2$)(acac$_2$en)]Cl to generate Re^{III} complexes of the type *trans*-[Re^{III}(PR$_3$)$_2$(acac$_2$en)]$^+$, **1** and **2**. The trialkylphosphine (PEt_3), however, resulted only in substitution to form the asymmetric *cis*-[Re^{V}O(PEt$_3$)(acac$_2$en)]$^+$ complex, **3**. This outcome was unexpected considering the increased basicity and reducing power of the trialkylphosphine. The triethylphosphine was expected to favor the formation of the Re^{III} complex relative to the aryl phosphines because of its strong reducing power. It is hypothesized that kinetics control this reaction; the rearrangement reaction is favored over oxygen atom abstraction for the more nucleophilic PEt_3. The reduction reaction is apparently not sufficiently facile compared to rearrangement situating the very nucleophilic PEt_3 cis to the oxo group. The resulting product, *cis*-[ReO(PEt$_3$)(acac$_2$en)]$^+$, appears resistant to subsequent reduction; use of a large excess of phosphine, higher temperatures, and different solvents resulted in the same product.

The reactions of *trans*-[ReOCl(acac$_2$pn)] with the three phosphine ligands yielded only the asymmetric *cis*-[Re^{V}O(PR$_3$)(acac$_2$pn)]$^+$ complexes, **4**−**6**. No reduced Re(III) complexes were detected in the reaction mixtures with the acac$_2$pn complexes. Attempts to convert the *cis*-[Re^{V}O(PR$_3$)(acac$_2$pn)]$^+$ complexes to the corresponding reduced compounds *trans*-[Re^{III}(PR$_3$)$_2$(acac$_2$pn)]$^+$ were unsuccessful, even with greater than a 10-fold excess of phosphine, higher reaction temperatures, and/or longer reaction times. Although the *trans*-[Re^{III}(PR$_3$)$_2$(acac$_2$en)]$^+$ complexes were not reacted with oxidants, exposure of solutions of these complexes to air did not appear to yield the *cis*-[Re^{V}O(PR$_3$)(acac$_2$pn)]$^+$ complexes as determined by NMR and color (red vs green).

General Characterization. Elemental analyses and electrospray ionization mass spectrometry (ESI-MS) of compounds **1**−**6** confirmed the identities of the products. The molecular ions with the expected rhenium isotope pattern were observed in the positive mode of ESI-MS. The FT-IR spectra of the Re(V) complexes showed the presence of the Re═O stretches between 960 and 970 cm^{-1}, typical of Re(V) monooxo complexes.[1−7,9−11] This band was absent in the spectra of the Re(III) complexes.

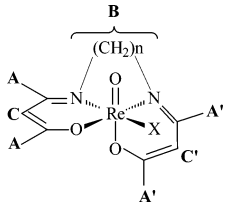
NMR Characterization. The asymmetric Re(V) products were easily characterized by their distinctive ^{1}H NMR spectra, with virtually all protons unique in these complexes. The acac$_2$en/pn ligands in *cis*-[Re^{V}O(PR$_3$)(L)]$^+$, compounds **3**−**6**, exhibit characteristic asymmetric splitting patterns (Table 3). Analysis of the ^{1}H NMR spectra can be divided on the basis of the orientation of the N, O donors relative to the Re(V) oxo group: one acac of acac$_2$en/pn is cis (or perpendicular) to the Re(V) oxo group while the second acac is parallel to the Re(V) oxo group. The acac moiety cis to the Re(V) oxo group exhibits chemical shifts for the methyl and vinyl protons similar to the Re(V) oxo starting materials *trans*-[ReOX(acac$_2$en/pn)]$^{0/+}$. The signals observed for the acac moiety parallel to the Re(V) oxo group were shifted dramatically (Table 3). The alkyl backbone, en or pn, in the asymmetric cis complexes showed increased splitting due to the inequivalency of these protons. Phosphorus coupling was observed in both the ^{1}H and ^{13}C NMR spectra. The aromatic carbons are assigned on the basis of the relative coupling constants expected for a quaternary P (assuming the Re as the fourth site) and the relative intensities of the signals.[20] The ^{31}P NMR chemical shifts for the coordinated phosphines were comparable in complexes **3**−**6** and observed as singlets between −15 and −17 ppm, a very narrow range considering that the free phosphines ranged from −5 to −20 ppm depending on the R groups (ca. −5 for triphenylphosphine and ca. −20 for triethylphosphine). The chemical shifts

(20) Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; John Wiley & Sons: New York, 1980.

Table 2. Selected Bond Angles (deg) and Distances (Å) for **1**−**5**

	1			3			5	
	molecule a	molecule b	2	molecule a	molecule b	4	molecule a	molecule b
Re−N1	2.041(4)	2.045(4)	2.0381(18)	2.070(5)	2.059(6)	2.095(3)	2.091(3)	2.084(3)
Re−N2	2.039(4)	2.044(4)	2.0381(18)	2.034(6)	2.025(6)	2.081(3)	2.084(3)	2.088(3)
Re−O1	2.027(3)	2.037(3)	2.0226(15)	2.021(4)	2.029(5)	2.026(3)	2.024(3)	2.032(3)
Re−O2	2.028(3)	2.025(3)	2.0226(15)	2.078(4)	2.079(5)	1.998(2)	2.010(3)	2.019(3)
Re−O3				1.692(5)	1.687(5)	1.688(3)	1.691(3)	1.690(3)
Re−P1	2.4827(11)	2.4992(11)	2.4579(8)	2.4860(18)	2.484(2)	2.5252(9)	2.478(1)	2.492(1)
Re−P2	2.4868(11)	2.4820(11)	2.4579(8)					
O1−Re−O2	98.41(13)	98.58(12)	94.79(9)	80.92(18)	81.33(19)	83.89(10	86.52(11)	84.24(11)
O1−Re−N1	89.66(15)	89.60(14)	91.12(7)	90.84(19)	90.2(2)	89.91(11)	88.82(12)	89.33(12)
O1−Re−N2	171.82(14)	172.65(13)	174.10(7)	158.2(2)	158.8(2)	166.76(11)	168.48(12)	167.08(12)
O1−Re−O3				102.2(2)	101.9(2)	99.74(11)	99.18(13)	98.04(13)
O1−Re−P1	86.63(9)	84.13(9)	88.64(4)	85.98(13)	87.58(14)	89.69(8)	84.92(8)	86.60(8)
O1−Re−P2	88.60(9)	87.56(9)	87.98(4)					
O2−Re−N1	171.34(15)	171.44(13)	174.10(7)	91.03(19)	91.4(2)	88.98(11)	86.06(11)	86.89(11)
O2−Re−N2	89.33(15)	88.64(14)	91.12(7)	80.3(2)	80.4(2)	83.04(11)	82.93(11)	83.06(12)
O2−Re−O3				166.2(2)	166.4(2)	168.96(11)	167.63(12)	168.65(12)
O2−Re−P1	91.43(9)	91.64(9)	87.98(4)	83.01(13)	83.45(14)	86.71(8)	85.24(7)	84.09(8)
O2−Re−P2	86.59(9)	87.02(9)	88.64(4)					
N1−Re−N2	82.77(16)	83.25(15)	82.98(11)	78.5(2)	79.6(2)	87.73(12)	85.86(12)	87.56(13)
N1−Re−O3				102.3(2)	101.7(2)	101.40(12)	104.92(13)	104.21(13)
N1−Re−P1	92.18(11)	91.70(10)	92.03(5)	173.62(16)	174.70(16)	175.69(8)	169.57(9)	170.44(9)
N1−Re−P2	90.50(11)	90.84(10)	91.72(5)					
N2−Re−O3								
N2−Re−P1	90.56(11)	94.33(10)	91.72(5)	102.65(17)	100.93(17)	91.69(9)	98.75(9)	94.49(10)
N2−Re−P2	94.53(11)	94.25(10)	92.03(5)					
O3−Re−P1				83.81(16)	83.48(17)	82.90(9)	84.35(9)	84.94(10)
P1−Re−P2	174.51(4)	171.29(4)	175.00(3)					

Table 3. ^{1}H NMR Spectral Assignments for **3**−**6** ($CDCl_3$, TMS, 500 MHz, Room Temperature)



	A/A (ppm)	**B** (ppm)	**C/C** (ppm)	X
3 ($n = 2$)	2.21 (s, 3H)	3.59−3.73 (m, 2H, CH_2CH_2)	5.45 (s, 1H)	1.02−1.15 (d of t, 9H, PCH_2CH_3)
	2.25 (s, 3H)	4.00−4.07 (m, 1H, CH_2CH_2)	6.06 (s, 1H)	
	2.34 (s, 3H)	5.29−5.41 (m, 1H, CH_2CH_2)		1.67−1.82 (m, 6H, PCH_2CH_3)
	3.02 (s, 3H)			
4 ($n = 3$)	1.73 (s, 3H)	2.01−2.20 (m, 2H, $CH_2CH_2CH_2$)	5.35 (s, 1H)	7.40−7.63 (m, 15H, PPh_3)
	2.21 (s, 3H)	3.12−3.19 (m, 1H, $CH_2CH_2CH_2$)	5.58 (s,1H)	
	2.29 (s, 3H)	3.48−3.61 (m, 1H, $CH_2CH_2CH_2$)		
	2.83(s, 3H)	4.21−4.27 (m, 1H, $CH_2CH_2CH_2$)		
		4.93−5.04 (m, 1H, $CH_2CH_2CH_2$)		
5 ($n = 3$)	1.52 (s, 3H)	2.35−2.42 (m, 2H, $CH_2CH_2CH_2$)	5.30 (s, 1H)	0.96−1.10 (d of t, 6H, PCH_2CH_3)
	2.18 (s, 3H)	3.08−3.19 (m, 1H, $CH_2CH_2CH_2$)	5.76 (s, 1H)	
	2.39 (s, 3H)	3.66−3.75 (m, 1H, $CH_2CH_2CH_2$)		1.84−2.23 (m, 4H, PCH_2CH_3)
	2.94 (s, 3H)	4.15−4.24 (m, 1H, $CH_2CH_2CH_2$)		
		4.99−5.10 (m, 1H, $CH_2CH_2CH_2$)		7.40−7.61 (m, 5H, PPh)
6 ($n = 3$)	2.16 (s, 3H)	1.97−2.10 (m, 2H, $CH_2CH_2CH_2$)	5.23 (s, 1H)	1.01−1.15 (d of t, 9H, PCH_2CH_3)
	2.23 (s, 3H)	3.07−3.18 (m, 1H, $CH_2CH_2CH_2$)	6.00 (s, 1H)	
	2.30 (s, 3H)	3.72−3.81 (m, 1H, $CH_2CH_2CH_2$)		1.61−1.81 (m, 6H, PCH_2CH_3)
	3.22 (s, 3H)	4.12−4.19 (m, 1H, $CH_2CH_2CH_2$)		
		5.11−5.20 (m, 1H, $CH_2CH_2CH_2$)		

of monodentate phosphines coordinated to metal centers can be affected by several factors including the oxidation state of the metal, the geometry of the metal complex, the steric bulk of the phosphine, and the chemical shift of the uncoordinated phosphine. These various factors may have additive, subtractive, or canceling effects on the chemical shift of the coordinated phosphine. The general tendency observed is that shielded ligands become less shielded on coordination (PEt_3 is the most shielded phosphine in our study), while deshielded ligands become more shielded (PPh_3 is the least shielded phosphine in our study).[21] Additionally, the higher the oxidation state of the metal center (+5 here) is, the greater sensitivity of the chemical shift of the coordinated phosphine, and shielding tends to increase as the group is descended.[21] Some combination of these various effects results in the coincidental narrow range of ^{31}P NMR

(21) Mason, J., Ed. *Multinuclear NMR*; Plenum Press: New York, 1987; pp 385−389.

Table 4. ^{1}H NMR Spectral Assignments for **1** and **2** ($CDCl_3$, TMS, 500 MHz, Room Temperature)

	Assgnt	δ (ppm)	mult; J (Hz)	integratn
1	ortho H (P−Ph)	+6.36	br s	12 H
	meta H (P−Ph)	+7.28	t; 7.3	12 H
	para H (P−Ph)	+8.88	t; 7.6	6 H
	NCH_2CH_2N	+40.71	s	4 H
	acac CH_3	−13.36, −29.50	2 s	6 H + 6 H
	acac CH	−13.50	br s	2 H
2	ortho H (P−Ph)	+12.51	d; 6.85	4 H
	meta H (P−Ph)	+7.09	t; 7.5	4 H
	para H (P−Ph)	+8.92	t; 7.3	2 H
	NCH_2CH_2N	+45.09	s	4 H
	P$CH_2$$CH_3$	+4.60, +1.71	2 v br s	4 H + 4 H
	PCH_2CH_3	+2.88	br m	12 H
	acac CH_3	−11.26, −27.60	2 s	6 H + 6 H
	acac CH	−12.30	br s	2 H

chemical shifts observed in these Re(V) complexes. The PPh_3 became significantly more shielded on coordination to Re(V) (−17.01 ppm vs −4.45 ppm) and also has the longest Re(V)−P bond distance (2.5252(9) Å) (ca. 2.48−2.49 Å for the PEt_3 and PEt_2Ph analogues, which became less shielded on coordination; Table 2). Other Re(V) complexes in which a phosphine group is cis to the oxo group show the expected variation in chemical shifts on coordination (i.e., are as variable as are their free phosphines).[22−26]

The paramagnetic d^4 Re^{III} metal center of **1** and **2** increased the complexity of the ^{1}H and ^{13}C NMR spectra and made them more difficult to interpret. The ^{1}H NMR spectra of the Re(III) complexes exhibited sharp signals; however, the chemical shifts were observed in an expanded window of about −30 to +50 ppm (Table 4), consistent with previously reported paramagnetic Re(III) complexes.[27−36] The aromatic protons of the coordinated phosphine are observed between 6.2 and 13 ppm. The ortho protons for *trans*-[$Re(PEt_2Ph)_2(acac_2en)$]PF_6 are split into a doublet and observed at 12.51 ppm, while the ortho protons for *trans*-[$Re(PPh_3)_2(acac_2en)$]PF_6 are observed as a broad singlet at 6.36 ppm (on the basis of the integration). The former is consistent with other Re(III)−PPh_3 reports while the latter is not.[27−37] ^{1}H−^{1}H COSY NMR spectra were used to confirm the assignments of the ortho, meta, and para protons, with cross correlation peaks observed for the meta protons with both the ortho and para protons in each complex. The meta and para protons are observed as triplets in both compounds with coupling constants of ca. 7.3−7.5 Hz. The methylene and methyl protons of the coordinated PEt_2Ph do not exhibit the usual proton coupling (i.e., quartet and triplet) but rather are observed as two very broad singlets (4.55 and 1.27 ppm) for each methylene proton and a broad multiplet (2.86 ppm) for the methyl protons. Each methylene proton is chemically inequivalent, as previously reported for Re(III) coordination.[31] No ^{31}P coupling is observed. The paramagnetic Re(III) center results in very fast relaxation of the phosphorus center and, thus, loss of coupling.[27−30,32,36,37] The two $acac_2en$ methyl groups (−11 to −30 ppm) and the methine proton (ca. −13 ppm) are observed upfield from TMS while the backbone methylene protons are observed significantly downfield (ca. 40−50 ppm). The chemical shifts in the ^{13}C NMR spectra were observed between −3 and +280 ppm relative to TMS, and short acquisition times were required because of the very fast relaxation times due to the paramagnetic center. The aromatic C directly bound to the phosphorus was not observed, as also reported by Randall et al. for [$ReX_3(PR_2Ph)_3$].[37] The aromatic carbon signals were very weak. The phosphines coordinated to the paramagnetic Re(III) center were not observed by ^{31}P NMR, consistent with previously reported paramagnetic Re(III) complexes.[30,32−34]

Table 5. $E^{\circ\prime}$ Values for the Re(III) Complexes and Their Tc(III) Analogues[a,b]

Complex	redox couple	$E^{\circ\prime}$(Re)	$E^{\circ\prime}$(Tc)[14]	diff
[$M(PEt_2Ph)_2(acac_2en)$]PF_6	III/II	−1.431	−0.889	0.542
[$M(PEt_2Ph)_2(acac_2en)$]PF_6	III/IV	0.118	0.716	0.598
[$M(PPh_3)_2(acac_2en)$]PF_6	III/II	−1.575	−1.037	0.538
[$M(PPh_3)_2(acac_2en)$]PF_6	III/IV	−0.014	0.674	0.688

[a] Conditions: cyclic voltammetry in propylene carbonate, 0.1 M TEAP; Pt working electrode; Ag/AgCl reference electrode; Pt auxiliary electrode; scan rate of 100 mV/s. [b] $E^{\circ\prime}$ values in V.

Electrochemistry. The cyclic voltammograms of the Re(III) and Re(V) Schiff base phosphine complexes were determined for comparison with the Tc(III) analogues, which showed both reversible Tc(III)/Tc(IV) and Tc(III)/Tc(II) couples.[15,16] The Re(III) analogues exhibited the same two reversible couples as did the related Tc(III) complexes, with the $E^{\circ\prime}$ values about 600 mV more negative for the Re compounds (Table 5), indicating that they are more difficult to reduce than their Tc analogues. The CV for **2** is shown in Figure 2. The very negative values of the Re(III)/Re(II) couples indicate that in vivo reduction will not be accessible, as these values are significantly more negative (more difficult to reduce) than those for the $Tc^{III}Q12$ compounds that have been evaluated for human use.[15−19] Additionally, *trans*-[$Re(PEt_2Ph)_2(acac_2en)]^+$ is harder to reduce than the PPh_3 analogue, as would be expected (the more electron-withdrawing triphenylphosphine groups allows for a more facile reduction) while it will be easier to oxidize than the PPh_3 analogue (increased σ-electron density on the phos-

(22) Bolzati, C.; Porchia, M.; Bandoli, G.; Boschi, A.; Malago, E.; Uccelli, L. *Inorg. Chim. Acta* **2001**, *315*, 205−212.
(23) Mazzi, U.; Refosco, F.; Bandoli, G.; Nicolini, M. *Transition Met. Chem.* **1985**, *10*, 121−127.
(24) Connac, F.; Lucchese, Y.; Dartiguenave, M.; Beauchamp, A. L. *Inorg. Chem.* **1997**, *36*, 256−259.
(25) Cavell, R. G.; Hilts, R. W.; Luo, H.; McDonald, R. *Inorg. Chem.* **1999**, *38*, 897−905.
(26) Nock, B.; Maina, T.; Tisato, F.; Papadopoulos, M.; Raptopoulou, C. P.; Terzis, A.; Chiotellis, E. *Inorg. Chem.* **1999**, *38*, 4197−4202.
(27) Shaw, D.; Randall, E. W. *J. Chem. Soc., Chem. Commun.* **1965**, 82−83.
(28) Randall, E. W.; Shaw, D. *Mol. Phys.* **1965**, *10*, 41−48.
(29) Chatt, J.; Leigh, G. J.; Mingos, D. M. P.; Randall, E. W.; Shaw, D. *J. Chem. Soc., Chem. Commun.* **1968**, 419−420.
(30) Randall, E. W.; Shaw, D. *J. Chem. Soc. A* **1969**, 2867−2872.
(31) Rossi, R.; Duatti, A.; Magon, L.; Casellato, U.; Graziani, R.; Toniolo, L. *J. Chem. Soc., Dalton Trans.* **1982**, 1949−1952.
(32) Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 2181−2186.
(33) Over, D. E.; Critchlow, S. C.; Mayer, J. M. *Inorg. Chem.* **1992**, *31*, 4643−4648.
(34) Pearson, C.; Beauchamp, A. L. *Inorg. Chim. Acta* **1995**, *237*, 13−18.
(35) Tisato, F.; Refosco, F.; Bolzati, C.; Cagnolini, A.; Gatto, S.; Bandoli, G. *J. Chem. Soc., Dalton Trans.* **1997**, 1421−1427.
(36) Bhattacharyya, S.; Banerjee, S.; Drghangi, B. K.; Menon, M.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1999**, 155−159.
(37) Mitsopoulou, C. A.; Mahieu, N.; Motevalli, M.; Randall, E. W. *J. Chem. Soc., Dalton Trans.* **1996**, 4563−4566.

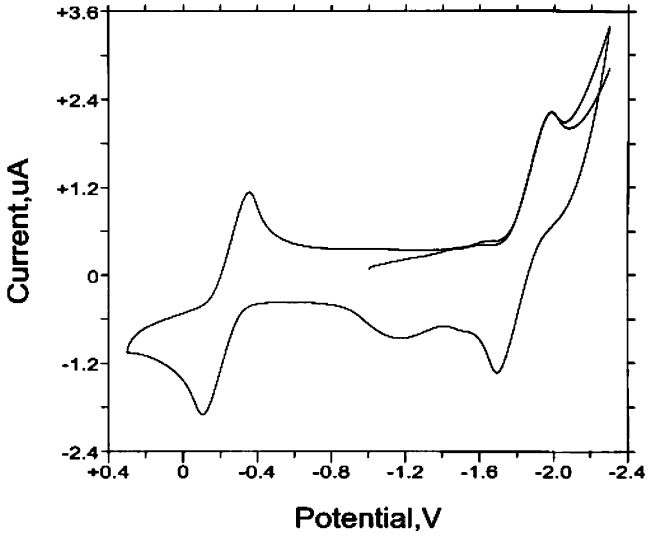


Figure 2. Cyclic voltammogram (CV) for *trans*-[$Re(PEt_2Ph)_2(acac_2en)$]-PF_6.

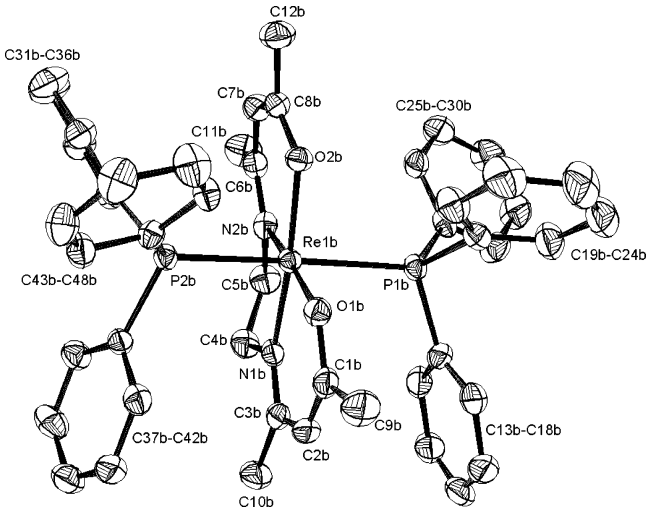


Figure 3. ORTEP representation of *trans*-[$Re^{III}(PPh_3)_2(acac_2en)]PF_6$, **1**, with 40% probability ellipsoids.

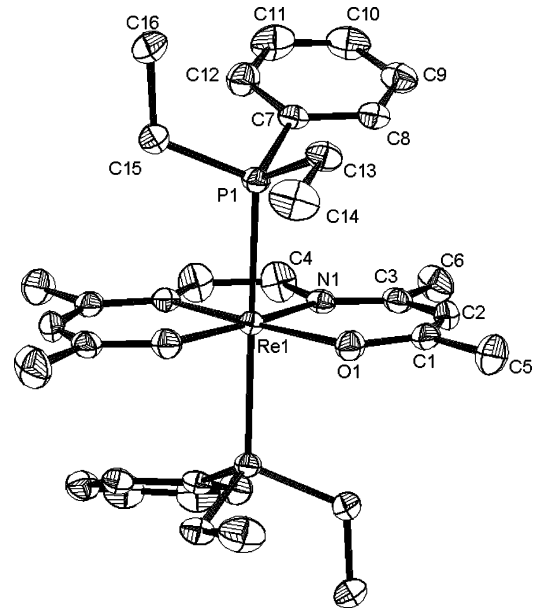


Figure 4. ORTEP representation of *trans*-[$Re^{III}(PEt_2Ph)_2(acac_2en)]PF_6$, **2**, with 40% probability ellipsoids.

phorus atom of PEt_2Ph makes the Re(III) complex easier to oxidize to the Re(IV) state). Another series of homologous Tc(III)/Re(III) phosphine complexes of the type *trans*-[MCl_2-(diphosphine)$_2$]$^+$ were reported to show reversible III/II and II/I redox couples, with the Re(III) couples about 200 mV more negative than the Tc(III) couples, while here about a 600 mV difference between analogous Tc and Re complexes was observed.[38]

The Re(V) complexes reported in our study were also evaluated electrochemically, but not surprisingly no reversible couples were observed. The Re(V) complexes contain an axial oxo group, which would most likely be lost on reduction to Re(IV) and thus result in a nonreversible Re(V)/Re(IV) couple. Oxidation of the Re(V) complexes might result in a Re(VI) complex or more likely the thermodynamically stable Re(VII) perrhenate. Very few Re(VI) complexes have been reported (mostly halide and oxide halide complexes)[39,40] and oxidation to Re(VI) may continue to Re(VII), in which case the couple would definitely be nonreversible. Both reduction to Re(IV) (loss of the oxo group) and oxidation to Re(VII) (octahedral to tetrahedral) would result in changes to the Re coordination sphere, making the process nonreversible.

X-ray Crystal Structures. The Re(III) complexes *trans*-[$Re(PPh_3)_2(acac_2en)]PF_6$, **1**, and *trans*-[$Re(PEt_2Ph)_2(acac_2$-en)]$PF_6$, **2**, and the Re(V) complexes *cis*-[$ReO(PEt_3)(acac_2$-en)]PF_6, **3**, *cis*-[$ReO(PPh_3)(acac_2pn)]PF_6$, **4**, and *cis*-[ReO-(PEt_2Ph)($acac_2pn$)]PF_6, **5**, were characterized by X-ray crystallography (Figures 3−7). The two Re(III) complexes are close to octahedral in geometry with the $acac_2$en ligand occupying the equatorial plane and two phosphine ligands trans to each other. The three Re(V) complexes are distorted octahedra with the Re═O group somewhat above the equatorial plane, as typically observed with Re(V) monooxo complexes, and the single phosphine ligand oriented cis to the Re═O group and with the trans oxo site occupied by a ligand ($acac_2$en/pn) oxygen.

***trans*-[Re(PPh_3)$_2$($acac_2$en)]PF_6 (1) and *trans*-[Re(PEt_2Ph)$_2$-($acac_2$en)]PF_6 (2).** The bond angles within the Re(III) complexes are near their expected values, with the angles for the cis and trans ligands approximately 82−98 and 171−174°, respectively, with the Re atoms in the ligand planes (Table 2).[41] The Re−O (2.0226−2.037 Å) and Re−N (2.038−2.045 Å) bond distances are consistent with the Re(V) oxo Schiff base complexes[3−6,8−11] and similar to other Re(III)−N and Re(III)−O bond distances.[42−45] The Re−P

(38) Kirchhoff, J. R.; Heineman, W. R.; Deutsch, E. *Inorg. Chem.* **1987**, *26*, 3108−3113.
(39) Housecroft, C. E.; Sharpe, A. G. *Inorganic Chemistry*; Prentice Hall: New York, 2001; pp 554−558.
(40) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 2nd ed.; Butterworth Heinemann: Oxford, U.K., 1997; pp 1040−1069.
(41) Available as Supporting Information.
(42) Lock, C. J. L.; Murphy, C. N. *Acta Crystallogr.* **1979**, *B35*, 951−954.
(43) Rossi, R.; Duatti, A.; Magon, L.; Casellato, U.; Graziani, R.; Toniolo, L. *J. Chem. Soc., Dalton Trans.* **1982**, 1949−1952.

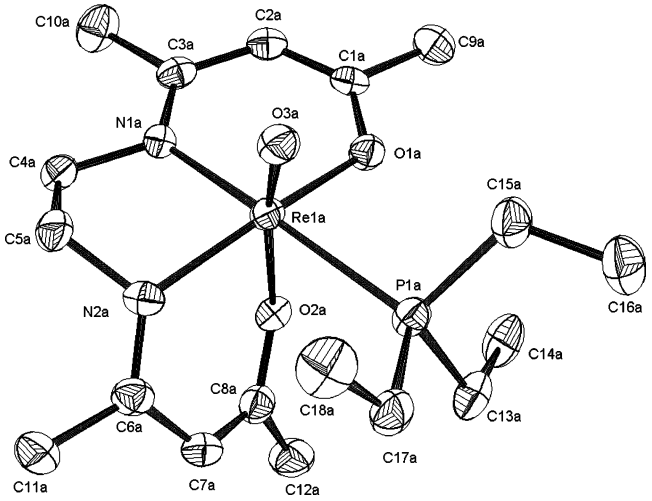


Figure 5. ORTEP representation of *trans*-[Re^{V}O(PEt$_3$)(acac$_2$en)]PF$_6$, **3**, with 40% probability ellipsoids.

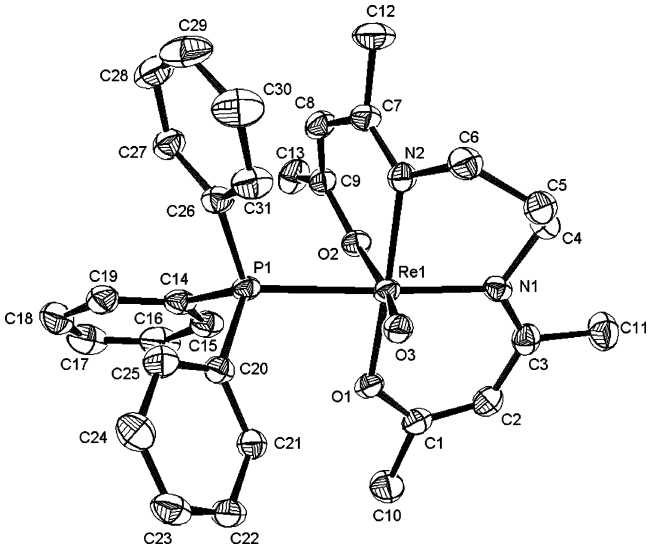


Figure 6. ORTEP representation of *trans*-[Re^{V}O(PPh$_3$)(acac$_2$pn)]PF$_6$, **4**, with 40% probability ellipsoids.

(2.4579−2.4992 Å) bond distances are comparable to those observed in other Re(III) complexes.[46−53] The near linear trans phosphine ligands (P−Re−P) are equidistant (2.45−2.49 Å) from the rhenium center. Two crystallographically unique complexes are observed in the unit cell of **1** with comparable bond angles and bond distances. The unit cell,

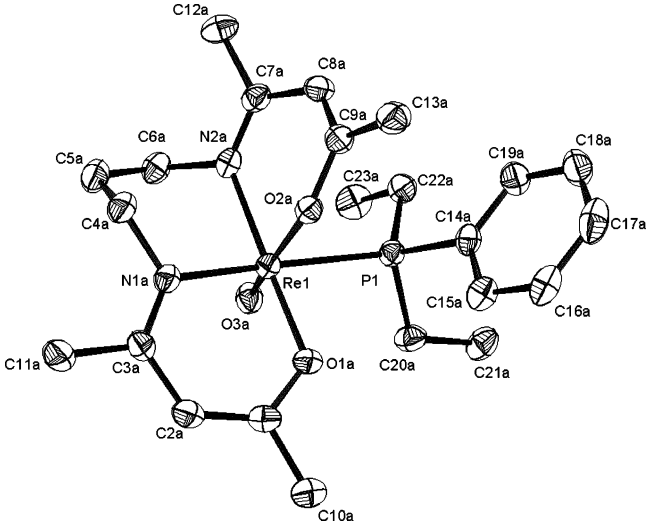


Figure 7. ORTEP representation of *trans*-[Re^{V}O(PEt$_2$Ph)(acac$_2$pn)]PF$_6$, **5**, with 40% ellipsoids.

bond angles, and bond distances of **1** are isostructural with those observed in the technetium analogue, *trans*-[^{99}Tc(acac$_2$-en)(PPh$_3$)$_2$]PF$_6$.[15] The bond distances of the Schiff base ligand (oxygen and nitrogen) to technetium ranged from 2.007 to 2.084 Å, and the trans phosphine ligands ranged from 2.499 to 2.511 Å,[15] very similar to those reported here for the Re(III) analogues.

***cis*-[ReO(PEt$_3$)(acac$_2$en)]PF$_6$ (3), *cis*-[ReO(PPh$_3$)(acac$_2$pn)]-PF$_6$ (4), and *cis*-[ReO(PEt$_2$Ph)(acac$_2$pn)]PF$_6$ (5).** The X-ray crystal structures of **3**−**5** illustrate the asymmetric coordination of the acac$_2$en or acac$_2$pn ligand resulting from the coordination of the phosphine ligand cis to the Re(V) oxo group (Figures 5−7). Complexes **3**−**5** exhibit distorted octahedral coordination geometry with the rhenium lying above the equatorial ligand plane (0.2 Å) toward the oxo group with the bond angles about the Re center ranging from 82 to 104° (cis) and 167 to 175° (trans). One oxygen and two nitrogen donor atoms from the tetradentate Schiff base ligand occupy three equatorial coordination sites, while the remaining oxygen donor coordinates in the axial position trans to the Re(V) oxo group. The Re−O bond distances for the equatorial oxygen atoms (2.010−2.026 Å) are comparable to those for the axial oxygen (1.998−2.078 Å) atoms. The Re−O, Re−N, and Re═O (1.688−1.692 Å) bond distances are comparable to those observed in other Re(V) complexes.[3−6,8−11,22,23] The Re(V) oxo core (O═Re−O) in **3**−**5** deviates slightly from linear (166.2−168.96°) due to ligand constraints from the asymmetric coordination. The Re−P bond distances in **3**−**5** (2.478−2.525 Å) are typical for Re(V) oxo cis phosphine complexes (2.39−2.55 Å).[11,13−17,22,23]

Reactivity of Phosphines with *trans*-[ReOX(Schiff base)] Complexes. The reactivity of monodentate phosphine ligands with the Re(V) complexes, *trans*-[ReOX(Schiff base)]$^{0/+}$, was investigated with the intent of generating the Re(III) complexes, *trans*-[Re(PR$_3$)$_2$(Schiff base)]$^{+}$, analogous to the Tc(III) complexes previously reported.[15,19] Rhenium(III) complexes should be more kinetically inert to substitution than Re(V) complexes and, thus, may yield more stable $^{186/188}$Re complexes under in vivo conditions, and Re(III) is reasonably

(44) Rall, J.; Weingart, F.; Ho, D. M.; Heeg, M. J.; Tisato, F.; Deutsch, E. *Inorg. Chem.* **1994**, *33*, 3442−3451.
(45) Fortin, S.; Beauchamp, A. L. *Inorg. Chem.* **2001**, *40*, 105−112.
(46) Duckworth, C. F.; Douglas, P. G.; Mason, R.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1970**, 1083−1084.
(47) Vanderheyden, J.-L.; Heeg, M. J.; Deutsch, E. *Inorg. Chem.* **1985**, *24*, 1666−1673.
(48) Pombeiro, A. J. L.; Hughes, D. L.; Pickett, C. J.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1986**, 246−247.
(49) Bakir, M.; Fanwick, P. E.; Walton, R. A. *Polyhedron* **1987**, *6*, 907−913.
(50) Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 2181−2186.
(51) Chang, L.; Aizawa, S.-I.; Heeg, M. J.; Deutsch, E. *Inorg. Chem.* **1991**, *30*, 4920−4927.
(52) Coutinho, B.; Dilworth, J. R.; Jobanputra, P.; Thompson, R. M.; Schmid, S.; Strahle, J.; Archer, C. M. *J. Chem. Soc., Dalton Trans.* **1995**, 1663−1669.
(53) Luo, H.; Liu, S.; Rettig, S. J.; Orvig, C. *Can. J. Chem.* **1995**, *73*, 2272−2281.

accessible from perrhenate, the starting compound on the radiotracer level. Although it was anticipated that the Re(V) complexes would be more difficult to reduce to Re(III) than their Tc(V) analogues, the formation of *cis*-[ReO(PEt$_3$)(acac$_2$en)]$^+$ was unexpected since the less nucleophilic and less reducing phosphines, PPh$_3$ and PEt$_2$Ph, resulted in the formation of the Re(III) complexes while the PEt$_3$ resulted in the formation of the asymmetric cis Re(V) oxo complex. Re(V) complexes with phosphine ligands bound cis to the Re(V) oxo group are known. Mazzi et al. reported Re(V) oxo complexes with a tridentate ONO Schiff base in which a tertiary phosphine was coordinated cis to the oxo group, as we observed for some of the Re(V) oxo tetradentate Schiff base complexes.[23] Softer σ donors, such as phosphines, prefer coordinating cis to the oxo group as observed with other Re(V) complexes.[22−26,54−58]

The reactions of tertiary phosphines with *trans*-[Re^{V}OX(Schiff base)]$^{0/+}$ complexes may involve initial loss of the labile water or chloride group trans to the oxo group, followed by formation of a 5-coordinate intermediate. This intermediate then rearranges on reaction with phosphine to give the *cis*-Re(V) product or it undergoes phosphine coordination, either trans to the oxo group or on the oxo group to yield the *trans*-Re(III) product on reaction with an additional 2 equiv of phosphine. One possible mechanism to the Re(III) product involves formation of a coordinated phosphine oxide followed by phosphine coordination trans to this group, loss of the phosphine oxide, and then finally coordination of the third 1 equiv of phosphine to yield the final product. A second possible mechanism involves initial phosphine coordination trans to the oxo group followed by attack of the second phosphine on the coordinated oxo group to form the coordinated phosphine oxide, loss of the phosphine oxide, and finally coordination of the third 1 equiv of phosphine to yield the Re(III) product. Whether oxygen atom abstraction and reduction to Re(III) occurs or whether rearrangement of the coordinated phosphine to the more favorable position cis to the oxo group occurs is most likely a kinetic phenomenon. When acac$_2$pn is the Schiff base, sufficient flexibility in the backbone allows the rearrangement reaction to be facile, and the resultant product is exclusively *cis*-[ReO(PR$_3$)(acac$_2$pn)]$^+$. This is consistent with the reports of the reaction of other Re(V) oxo complexes with phosphines.[22−26,54−58] When acac$_2$en is coordinated to the Re(V) oxo complex, the coordinated Schiff base ligand is quite rigid and the reduction reaction is sufficiently facile to compete favorably with the rearrangement reaction. However, when PEt$_3$ coordinates trans to the oxo group, the reduction reaction is not favored. The major product (85−90% on the basis of NMR) is the rearranged Re(V) oxo complex, *cis*-[ReO(PEt$_3$)(acac$_2$en)]$^+$, even though PEt$_3$ is the strongest reducing agent and the best oxygen atom abstractor of the phosphines investigated. Triethylphosphine is also the strongest nucleophile, and because of its strong σ-donating and π-back-bonding characteristics (or tendencies), the reduction reaction is not able to effectively compete with the rearrangement reaction thus yielding the Re(V) product.

The pathway to the Re(III) complexes is probably similar to the phosphine oxygen abstraction mechanism proposed for the analogous technetium complexes.[15] The mechanism suggested involves a three-step process: coordination of a phosphine in the labile position trans to the oxo moiety; abstraction of the oxo group by a second phosphine; coordination of a third phosphine in the position originally occupied by the yl oxygen. The surprising observations for *trans*-[ReO(OH$_2$)(acac$_2$en)]$^+$ are that triphenylphosphine and diethylphenylphosphine reduce the Re(V) core to Re(III) while triethylphosphine does not, perhaps due to the weaker σ donation of the former phosphines compared to triethylphosphine, possibly allowing coordination trans to the oxo group followed by oxygen atom abstraction and reduction, or to steric interaction(s) of the aryl group(s) inhibiting rearrangement. In the Tc system all of the phosphines investigated resulted in the formation of Tc(III) bis(phosphine) complexes,[15,17] consistent with the more facile reduction of Tc(V) compared to Re(V).

Conclusions

The reactions of tertiary phosphine ligands with the Re(V) oxo Schiff base complexes, *trans*-[ReOX(acac$_2$en/pn)]$^{0/+}$, result in either the reduced and disubstituted Re^{III} product, *trans*-[Re^{III}(PR$_3$)$_2$(acac$_2$en)]$^+$, or the Re^V monosubstituted product, *cis*-[Re^{V}O(PR$_3$)(Schiff base)]$^+$. The nature of the phosphine ligand (i.e., alkyl or aryl) and the ligand backbone (i.e., en vs pn) determine the product formed, and the reaction path appears to be kinetically driven. This work demonstrates that it is possible to prepare Re(III) complexes of the type *trans*-[Re(PR$_3$)$_2$(Schiff base)]$^+$ with due consideration of the Schiff base ligand, possible steric effects, and the properties of the phosphine ligand. Extension of this chemistry to the radiotracer level is underway, with preliminary ^{186}Re radiotracer studies indicating that phosphine coordination prior to Schiff base complexation will probably be necessary at the radiotracer level (μM or less) rather than formation of the Re(V) Schiff base complex first, as is done in forming ^{99m}TcQ12. The Re(III) complexes will not be accessible to in vivo reduction, on the basis of their III/II redox potentials, and the strong σ-donating and π-back-bonding properties of the phosphines should stabilize Re(III) to oxidiation. Water-soluble, triarylphosphines may allow facile access to Re(III) and sufficiently decrease the lipophilicity of the resultant complexes to make them biologically compatible.

Experimental Section

General Considerations. Unless noted, all common laboratory chemicals were of reagent grade or better. Solvents were degassed with nitrogen gas prior to use, and all experiments were carried out under a nitrogen atmosphere unless otherwise noted. ^{1}H and

(54) Sacerdoti, M.; Bertolasi, V.; Gilli, G.; Duatti, A. *Acta Crystallogr.* **1984**, *C40*, 968−970.
(55) Battistuzzi, R.; Manfredini, T.; Battaglia, L. P.; Corradi, A. B.; Marzotto, A. *J. Crystallogr. Spectrosc. Res.* **1989**, *19*, 513−534.
(56) Gerber, T. I. A.; Perils, J.; Du Preez, J. G. H.; Bandoli, G. *Acta Crystallogr.* **1997**, *C53*, 217−219.
(57) Perez-Lourido, P.; Romero, J.; Garcia-Vazquez, J.; Sousa, A.; Maresca, K. P.; Rose, D. J.; Zubieta, J. *Inorg. Chem.* **1998**, *37*, 3331−3336.
(58) Chen, X.; Femia, F. J.; Babich, J. W.; Zubieta, J. *Inorg. Chim. Acta* **2000**, *307*, 149−153.

^{13}C NMR spectra were recorded on a Bruker 250 or 500 MHz instrument at 25 °C in deuterated chloroform with TMS as an internal reference. ^{31}P NMR spectra were recorded on a Bruker 250 MHz instrument at 25 °C in deuterated chloroform with H_3PO_4 as an external reference. Two-dimensional NMR correlation spectra were only obtained for the Re(III) complexes to allow chemical shift assignments, and only ^{1}H−^{1}H chemical shift correlation (COSY) experiments were run. All other NMR spectra were run in one-dimensional mode only. FT-IR spectra were obtained as KBr pellets on a Nicolet Magna-IR spectrometer 550. UV−vis spectra were recorded on a Hewlet Packard 8452A diode array spectrophotometer. Electrospray ionization mass spectra (ESI-MS) were obtained on a Thermo Finnigan TSQ7000 triple-quadrupole instrument with an API2 source. Elemental analyses were performed by Quantitative Technologies Inc. (QTI; Whitehouse, NJ).

Materials. 2,4-Pentanedione, 1,2-ethylenediamine, and 1,3-propylenediamine were purchased from Aldrich and used without further purification. The ligands, $\mathbf{L_1}$ = *N*,*N*′-ethylenebis(acetylacetone imine) ($acac_2en$) and $\mathbf{L_2}$ = *N*,*N*′-propylenebis(acetylacetone imine) ($acac_2pn$) were prepared according to the previously reported methods.[59,60] Ligands ($\mathbf{L_1}$ and $\mathbf{L_2}$) were recrystallized prior to use from either absolute ethanol, dry isopropyl alcohol, hexane, or ethyl ether. Tetrabutylammonium tetrachlorooxorhenium(V) ([*n*-Bu_4N][Re^VOCl_4]) was prepared by bubbling anhydrous HCl(g) into an ethanol solution of n-$NBu_4[ReO_4]$ for 30 min at 25 °C; gold-orange crystals formed upon concentrating and then cooling the solution.[61] The purified complexes *trans*-[$Re^VO(OH_2)(acac_2en)$]Cl and *trans*-[$ReOCl(acac_2pn)$] were prepared as reported previously.[11]

***trans*-[$Re^{III}(PPh_3)_2(acac_2en)$][$PF_6$]·$H_2O$ (1). Method 1.** (*n*-Bu_4)[Re^VOCl_4] (50 mg, 0.085 mmol) was added to 20 mL of a degassed solution of $acac_2en$, $\mathbf{L_1}$ (42.5 mg, 0.189 mmol), in absolute ethanol, and the mixture was refluxed for 1.5 h under a nitrogen atmosphere. After 1.5 h, triphenylphosphine (89.1 mg, 0.34 mmol) dissolved in 2 mL of dichloromethane was added to the reaction vessel, and the resultant reaction mixture was refluxed for an additional 3 h to yield a red solution and a brown precipitate. The mixture was then cooled to room temperature and filtered, and the supernatant was evaporated to dryness in vacuo, to yield a product-containing residue. Purification of the complex was achieved by silica gel column chromatography. The reaction mixture was reconstituted in the minimum volume of dichloromethane and adsorbed on a column (1 cm × 20 cm) equilibrated in dichloromethane. The column was eluted with CH_2Cl_2 until a yellow band (containing triphenylphosphine) was removed. The eluent was then changed to acetone, which eluted several unidentified bands. The desired red product was finally displaced with methanol. After addition of tetrabutylammonium hexafluorophosphate (*n*-Bu_4NPF_6) (36.3 mg, 0.094 mmol), the solution was filtered and the filtrate concentrated to ∼5 mL and placed in the freezer for several days. Dark red X-ray-quality crystals of **1** were collected by filtration and washed with three 5 mL aliquots of toluene, followed by three 5 mL aliquots of ether. Yield: 48% (45 mg).

Method 2. Triphenylphosphine (45.0 mg, 0.172 mmol) in 2 mL of degassed dichloromethane was added to *trans*-[$Re^VO(OH_2)(acac_2en)$]Cl (25 mg, 0.0523 mmol) in 10 mL of degassed absolute ethanol. The solution was refluxed overnight and then cooled to room temperature. The reaction mixture was purified by silica gel chromatography as indicated in method 1. Yield: 82% (∼45 mg). ^{1}H NMR [$CDCl_3$, 500 MHz; δ (ppm)]: −29.50 (s; 6 H; acac CH_3); −13.50 (br s; 2 H; acac CH); −13.36 (s; 6 H; acac CH_3); 6.36 (br s; 12 H; ortho H); 7.28 (t; J = 7.3 Hz; 12 H; meta H); 8.88 (t; J = 7.6 Hz; 6 H; para H); 40.71 (s; 4H; NCH_2CH_2N). ^{13}C NMR [$CDCl_3$, 500 MHz; δ (ppm)]: 118.99, 126.07 (acac CH_3), 126.82 (acac CH_3), 132.07, 132.77, 133.63, 133.78, 141.34 (NCH_2CH_2N), 174.66, 275.69. UV−vis [CH_2Cl_2, λ in nm (ϵ in cm^{-1} M^{-1})]: 238 (27 970), 280 sh (13 400), 378 (5990), 422 (8320), 538 (1520). MS (*m*/*z*): [M+] 933, 935; calcd 931.81, 933.81. Anal. Calcd (found) for $ReC_{48}H_{48}N_2O_2P_3F_6$: C, 53.48 (53.48); H, 4.46 (4.25); N, 2.60 (2.47); P, 8.64 (8.48); F, 10.58 (10.39).

***trans*-[$Re^{III}(PEt_2Ph)_2(acac_2en)$][$PF_6$] (2).** The synthesis of **2** followed the procedures described for method 2 of compound **1**, substituting diethyphenylphosphine in THF for triphenylphosphine in dichloromethane. Yield: 80% (37 mg). Recrystallization from CH_2Cl_2/hexane (1:1) by slow evaporation yielded X-ray-quality crystals. ^{1}H NMR [$CDCl_3$, 500 MHz; δ (ppm)]: −27.60 (s; 6 H; acac CH_3); −12.30 (br s; 2 H; acac CH); −11.26 (s; 6 H; acac CH_3); 1.71, 4.60 (2 v br s; 4 H; PCH_2); 2.80 (br s; 12 H; PCH_2CH_3); 7.09 (t; J = 7.5 Hz; 4 H; meta H); 8.92 (t; J = 7.3 Hz; 2 H; para H); 12.51 (d; J = 6.85 Hz; 4 H; ortho H); 45.09 (s; 4 H; NCH_2CH_2N). ^{13}C NMR [$CDCl_3$, 500 MHz; δ (ppm)]: −2.52 (PCH_2CH_3), 117.72, 119.06, 120.09, 120.33 (acac CH_3), 123.16 (acac CH_3), 142.91 (NCH_2CH_2N), 161.78, 166.26 (PCH_2), 189.79. UV−vis [CH_2Cl_2, λ in nm (ϵ in cm^{-1} M^{-1})]: 234 (24 100), 264 (18 000), 382 (9010), 406 (8690), 428 (8650), 490 (1390), 530 (1160). MS (*m*/*z*): [M+] 739, 741; calcd 739.64, 741.64. Anal. Calcd (found) for $ReC_{32}H_{48}N_2O_2P_3F_6$: C, 43.39 (43.76); H, 5.42 (5.29); N, 3.16 (2.99); P, 10.51 (8.11); F, 12.88 (12.45).

***cis*-[$Re^VO(PEt_3)(acac_2en)$][PF_6] (3).** *trans*-[$ReO(OH_2)(acac_2en)$]-Cl (25 mg, 0.0523 mmol) was dissolved in 10 mL of absolute ethanol. Triethylphosphine (6.8 mg, 0.057 mmol) in THF was added to the reaction mixture. The solution was refluxed for 1 h followed by the addition of tetrabutylammonium hexaflurophosphate (NBu_4-PF_6) (22.3 mg, 0.058 mmol). The solution was filtered, concentrated to 2 mL by rotary evaporation, and cooled to −30 °C. Analytically pure dark brown X-ray-quality crystals of **3** were obtained after several days. Yield: 75% (27 mg). ^{1}H NMR [$CDCl_3$, 250 MHz; δ (ppm)]: 1.02−1.15 (PCH_2CH_3, d of t, 9H, J_{P-H} = 15.6 Hz); 1.67−1.82 (PCH_2CH_3, m, 6H); 3.59−3.73 (2H), 4.00−4.07 (1H), 5.29−5.41 (1H) (NCH_2CH_2N, m, 4H); 2.21, 2.25, 2.34, 3.02 ((CH_3)-CCHC(CH_3)O, four s, 12 H); 5.45, 6.06 ((CH_3)CCHC(CH_3)O, s, 2H). ^{13}C NMR [$CDCl_3$, 250 MHz; δ (ppm)]: 7.09, 7.14 (PCH_2CH_3; J_{P-C} = 3.1 Hz); 17.74, 18.17 (PCH_2CH_3 ; J_{P-C} = 27.5 Hz); 21.78, 23.96, 24.70, 25.73 ((CH_3)CCHC(CH_3)O); 59.06, 63.90 (NCH_2CH_2-N); 102.94, 109.80 ((CH_3)CCHC(CH_3)O); 175.40, 178.29 (−(CH_3)-**C**=N−); 184.43, 186.62 (−(CH_3)CO). ^{31}P NMR: −15.21 ppm. UV−vis [CH_2Cl_2, λ in nm (ϵ in cm^{-1} M^{-1})]: 232 (2200), 272 (2390), 346 (1420), 414 (936). IR (KBr, ν in cm^{-1}): 964 (Re═O). MS (*m*/*z*): [M+] 542, 544; calcd 541.39, 543.40. Anal. Calcd (found) for $ReC_{18}H_{33}N_2O_3P_2F_6$: C, 31.44 (31.48); H, 4.80 (4.82); N, 4.08 (3.88); P, 9.02 (9.08); F, 16.59 (16.59).

***cis*-[$Re^VO(PPh_3)(acac_2pn)$][PF_6] (4).** *trans*-[$ReO(acac_2pn)Cl$] (25 mg, 0.053 mmol) was dissolved in 10 mL of degassed absolute ethanol. Triphenylphosphine (15.2 mg, 0.058 mmol) dissolved in 2 mL of degassed dichloromethane was added to the reaction vessel. The solution was heated for ca. 1 h under a nitrogen atmosphere. Tetrabutylammonium hexafluorophosphate (*n*-Bu_4NPF_6) (22.4 mg, 0.058 mmol) was then added to the reaction mixture while the solution was still warm. Upon cooling of the sample to room

(59) McCarthy, P. J.; Hovey, R. J.; Ueno, K.; Martell, A. E. *J. Am. Chem. Soc.* **1955**, *77*, 5820−5824.
(60) Lindoy, L. F.; Lip, H. C.; Moody, W. E. *J. Chem. Soc., Dalton Trans.* **1974**, 44−47.
(61) Alberto, R.; Schibli, R.; Egli, A.; Schubiger, A.; Herrmann, W.; Artus, G.; Abram, W.; Kaden, T. *J. Organomet. Chem.* **1995**, *492*, 217−224.

temperature, a green precipitate **4** resulted. The product was collected by filtration and washed with three 5 mL aliquots of toluene, followed by three 5 mL aliquots of cold ethanol and finally three 5 mL aliquots of ether. Yield: >99% (46 mg) based on the starting material *trans*-[ReOCl(acac$_2$pn)]. X-ray-quality crystals of **4** were obtained by slow crystallization of a concentrated solution of ethanol/chloroform (1:1) in the freezer. ^{1}H NMR [$CDCl_3$, 250 MHz; δ (ppm)]: 2.01−2.20 ($NCH_2CH_2CH_2$, m, 2H); 1.73, 2.21, 2.29, 2.83 ((CH_3)CCHC(CH_3)O, four s, 12 H); 3.12−3.19, 3.48−3.61, 4.21−4.27, 4.93−5.04 ($NCH_2CH_2CH_2$, 4 m, 4H); 5.35, 5.58 ($(CH_3)CCHC(CH_3)O$, two s, 2H); 7.40−7.46, 7.55−7.62 (P*Ph*, 2 m, 15H). ^{13}C NMR [$CDCl_3$, 250 MHz; δ (ppm)]: 21.98, 22.29, 24.37, 25.26 ((CH_3)CCHC(CH_3)O); 27.12 ($NCH_2CH_2CH_2N$); 50.98, 56.82 ($NCH_2CH_2CH_2N$); 104.99, 107.69 ($(CH_3)CCHC(CH_3)O$); 128.75 and 128.92 (P*Ph*; J_{C-P} 10.2 Hz, meta), 130.79 and 131.538 (J_{P-C} 47.2 Hz, PC), 131.28 and 131.31 (J_{P-C} 2.2 Hz, para), 133.52 and 133,68 (J_{P-C} 10.0 Hz, ortho); 172.99, 177.28 ($(CH_3)C$=N−); 177.69, 184.60 (−$(CH_3)CO$). ^{31}P NMR: −17.10 ppm. UV−vis [CH_2Cl_2, λ in nm (ϵ in cm^{-1} M^{-1})]: 238 (21 540), 274 (12 774), 344 (4790). MS (*m*/*z*): [M+] 699, 701; calcd 699.55, 701.55. IR (KBr, ν in cm^{-1}): 960 (Re=O). Anal. Calcd (found) for $ReC_{31}H_{35}N_2O_3P_2F_6$: C, 44.02 (43.88); H, 4.14 (4.01); N, 3.31 (3.28); P, 7.34 (7.82); F, 13.49 (13.34).

***cis*-[Re^{V}O(PEt$_2$Ph)(acac$_2$pn)][PF$_6$] (5).** The synthesis and purification of **5** followed the procedure described for compound **4**, substituting diethylphenylphosphine for triphenylphosphine. Yield: >99% (40 mg). ^{1}H NMR [$CDCl_3$, 250 MHz; δ (ppm)]: 0.90−1.10 (PCH_2CH_3, d of t, 6H); 1.84−2.25 (PCH_2CH_3, 2 complex m, 4H); 1.86−1.99 ($NCH_2CH_2CH_2$, m, 2H); 1.52, 2.18, 2.39, 2.94 ((CH_3)CCHC(CH_3)O, 4 s, 12 H); 3.08−3.19, 3.66−3.75, 4.15−4.24, 4.99−5.10 ($NCH_2CH_2CH_2$, 4 m, 4H); 5.30, 5.76 ($(CH_3)CCHC(CH_3)O$, 2 s, 2H); 7.44−7.61 (P*Ph*Et$_2$, m, 5H). ^{13}C NMR [$CDCl_3$, 250 MHz; δ (ppm)]: 6.78, 6.86, 7.00, 7.04 (PCH_2CH_3, 2 d); 17.81, 18.16, 18.26, 18.61 (PCH_2CH_3, 2 d); 21.52, 22.20, 24.27, 25.35 ((CH_3)CCHC(CH_3)O); 27.44 ($NCH_2CH_2CH_2N$); 50.49, 56.60 ($NCH_2CH_2CH_2N$); 104.60, 108.16 ($(CH_3)CCHC(CH_3)O$); 128.82 and 129.55 (J_{P-C} 45.4 Hz, PC), 128.92 and 129.07 (J_{P-C} 9.4 Hz, meta), 130.79 and 130.83 (J_{P-C} 2.4 Hz, para), 131.54 and 131.67 (J_{P-C} 7.9 Hz, ortho) (P*Ph*Et$_2$, 4 d); 172.68, 177.99 ($(CH_3)C$=N−); 179.30, 185.05 ($(CH_3)CO$). ^{31}P NMR: −15.82 ppm. UV−vis [CH_2Cl_2, λ in nm (ϵ in cm^{-1} M^{-1})]: 234 (16 150), 276 (11 590), 346 (5130). MS (*m*/*z*): [M+] 603, 605; calcd 603.46, 605.47. IR (KBr, ν in cm^{-1}): 967 (Re=O). Anal. Calcd (found) for $ReC_{23}H_{35}N_2O_3P_2F_6$: C, 36.85 (36.73); H, 4.67 (4.50); N, 3.74 (3.64); P, 8.28 (8.32); F, 15.22 (15.02).

***cis*-[Re^{V}O(PEt$_3$)(acac$_2$pn)][PF$_6$] (6).** The synthesis and purification of **6** followed the procedure outlined in method 2 for compound **4**, substituting triethylphosphine for triphenylphosphine with slight modifications. After the reaction mixture was refluxed and the *n*-Bu_4NPF_6 added to the reaction mixture, the solution was concentrated to approximately 5 mL and then placed in the freezer overnight to yield green crystals that were collected and washed with three 5 mL aliquots of toluene and three 5 mL aliquots of ether. The crystals were analytically pure and required no additional purification. Yield: >99%. ^{1}H NMR [$CDCl_3$, 250 MHz; δ (ppm)]: 1.01−1.18 (PCH_2CH_3, d of t, 9H, J_{P-H} 15.7 Hz); 1.65−1.81 (PCH_2CH_3, m, 6H); 1.97−2.10 ($NCH_2CH_2CH_2$, m, 2H); 2.16, 2.23, 2.30, 3.22 ((CH_3)CCHC(CH_3)O, 4 s, 12H); 3.07−3.18, 3.72−3.82, 4.12−4.19, 5.11−5.20 ($NCH_2CH_2CH_2$, 4 m, 4H); 5.23, 5.99 ($(CH_3)CCHC(CH_3)O$, 2 s, 2H). ^{13}C NMR [$CDCl_3$, 250 MHz; δ (ppm)]: 6.88, 6.936 (PCH_2CH_3, d, J_{P-C} 3.7 Hz); 17.05, 17.49 (PCH_2CH_3, d, J_{P-C} 27.6 Hz); 19.47, 21.93, 23.65, 24.96 ((CH_3)CCHC(CH_3)O); 27.11 ($NCH_2CH_2CH_2N$); 49.56, 56.71 ($NCH_2CH_2CH_2N$); 104.47, 106.67 ($(CH_3)CCHC(CH_3)O$); 172.5, 177.5 (−$(CH_3)C$=N−); 178.5, 184.5 (−$(CH_3)CO$). ^{31}P NMR: −16.22 ppm. UV−vis [CH_2Cl_2, λ in nm (ϵ in cm^{-1} M^{-1})]: 212 (11 070), 274 (9960), 344 (4860). IR (KBr, ν in cm^{-1}): 967 (Re=O). MS (*m*/*z*): [M+] 555, 557; calcd 555.42, 557.42. Anal. Calcd (found) for $ReC_{19}H_{35}N_2O_3P_2F_6$: C, 32.52 (32.59); H, 4.99 (4.87); N, 3.99 (3.90); P, 8.84 (8.91); F, 16.26 (16.50).

Electrochemical Studies. Electrochemical data were obtained with a Bioanalytical Systems Inc. (BAS) CV-50 instrument. Tetraethylammonium perchlorate (TEAP; 0.1 M) in propylene carbonate (Burdick and Jackson, high-purity solvent for GC and spectrophotometry) was used as the electrolytic solution. A non-aqueous Ag/AgCl solution with 0.1 M TEAP in propylene carbonate was used as the reference electrode, in conjunction with Pt auxiliary and Pt working electrodes, for analyzing the Re complexes (1 mM). Ferrocene (3 mM in propylene carbonate) was used as a reference standard with a Ag/AgCl aqueous reference electrode.

X-ray Structure Determination and Refinement for 1−5. Intensity data were obtained at −100 °C on a Bruker SMART CCD area detector system using the ω scan technique with Mo Kα radiation from a graphite monochromator. Intensities were corrected for Lorentz and polarization effects. Equivalent reflections were merged, and absorption corrections were made using the multiscan method. Space group, lattice parameters, and other relevant information are given in Table 1. The structure was solved by direct methods with full-matrix least-squares refinement, using the SHELX package.[62,63] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms, except those of the waters of crystallization, were placed at calculated positions and included in the refinement using a riding model, with fixed isotropic *U*. The final difference map contained no features of chemical significance.

Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC048670J

(62) Sheldrick, G. M. *SHELXS-97, Crystal Structure Solution*; University of Gottingen: Gottingen, Germany, 1997.
(63) Sheldrick, G. M. *SHELXL-97, Crystal Structure Refinement*; University of Gottingen: Gottingen, Germany, 1997.